Oxygen Reduction Reaction for Generating H_2O_2 through a Piezo-Catalytic Process over Bismuth Oxychloride

Dengkui Shao,[a, b] Ling Zhang,[a] Songmei Sun,[a] and Wenzhong Wang*[a]

Oxygen reduction reaction (ORR) for generating H_2O_2 through green pathways have gained much attention in recent years. Herein, we introduce a piezo-catalytic approach to obtain H_2O_2 over bismuth oxychloride (BiOCl) through an ORR pathway. The piezoelectric response of BiOCl was directly characterized by piezoresponse force microscopy (PFM). The BiOCl exhibits efficient catalytic performance for generating H_2O_2 (28 mmol $h^{@1}$) only from O_2 and H_2O, which is above the aver-age level of H_2O_2 produced by solar-to-chemical processes. A piezo-catalytic mechanism was proposed: with ultrasonic waves, an alternating electric field will be generated over BiOCl, which can drive charge carriers (electrons) to interact with O_2 and H_2O, then to form H_2O_2.

H_2O_2 is widely used in pulp bleaching and disinfection,[1] furthermore, it has been explored as a green fuel for fuel cells in recent years.[2] However, the current industrial process of producing H_2O_2 involves anthraquinones in organic solvents and the H_2O_2 extracted from this system may be contaminated by organic impurities: Moreover, the direct synthesis of H_2O_2 from the reaction of H_2 and O_2 catalyzed by Pd or Pd/Au alloy is an alternative with risk of explosion.[3] The sustainable production of H_2O_2 from H_2O and O_2 through a solar-to-chemical process is therefore investigated owing to the sufficient and endless sunlight.[4] Small kinetic energies[5] such as those from sound, water waves, and vibrations are everywhere as well as solar energy, and they may be considered as other appealing driving forces for generating H_2O_2 through the oxygen reduction reaction (ORR).

With the rapid development of piezoelectric materials,[6] growing interest has been devoted to the conversion of mechanical energy into electricity or even chemical energy.[7] Numerous studies about nanogenerators that could harvest mechanical forces have been reported since Wang and Song reported a ZnO nanogenerator.[8] Moreover, there are increasing research works reporting the direct conversion of mechanical energy into chemical energy, which is termed as the piezo-electrochemical effect[7] or piezo-catalytic effect.[9] In a typical piezo-catalytic process, piezoelectric materials generate an electric field with external mechanical force, which can drive charge carriers (electrons and holes) participating in redox reactions such as water splitting[7,10] or elimination of pollutants.[9, 11, 12] Mechanistic analysis showed that H_2O_2 could be generated in situ in the electrochemical process.[13] However, in the process of pollutant degradation through the piezo-cata-lytic effect, H_2O_2 is overlooked or only regarded as one of the active species to remove the pollutants and the mechanism of generating H_2O_2 is unclear.

BiOCl has a layered structure and the $[Bi_2O_2]^{2+}$ and $Cl^{@}$ layers are stacked together by van der Waals force along the c-axis, and the structure provides a space large enough to induce a dipole along this direction.[14] It was verified that the internal electric field along <001 > was the intrinsic driving force for the spatial separation and transport of carriers in BiOCl.[15] Herein, we report that H_2O_2 was obtained by an ORR pathway over BiOCl with ultrasonic waves. The piezoelectric response of BiOCl was directly characterized by piezoresponse force microscopy (PFM). The controlled experiments under different atmospheres indicated that H_2O_2 originated mainly from the interaction of O_2 and H_2O. Reduction of Au^{3+} in the suspension of BiOCl with ultrasonic waves proved the existence of elec-trons. The addition of scavengers confirmed that the H_2O_2 was obtained from O_2 reduction by induced electrons. This work proposes a mechanism to explain the piezo-catalytic genera-tion of H_2O_2 and provides a clean and sustainable strategy for the production of H_2O_2 owing to the inorganic and safe pro-cess, and freely available O_2 and H_2O.

An SEM image of the hydrothermally synthesized BiOCl is shown in Figure 1 a. BiOCl exhibits a square-like morphology. The width of the as-prepared BiOCl is about 2–5 mm and the thickness is about 200–300 nm. Figure 1 b shows the crystal structure of BiOCl. All the peaks of BiOCl could be well indexed to the tetragonal phase of BiOCl with the lattice parameters of a =b =0.3891 nm and c =0.7369 nm (JCPDS No. 06-249).[16] These results show that the as-prepared BiOCl is well crystal-lized.

The piezoelectric response of BiOCl was characterized by an atomic force microscope (AFM) with a ferroelectric test system. Figure 2 shows the AFM and PFM images of the BiOCl micro-plates. The AFM image shows that the width of as-prepared BiOCl is about 3 mm and the thickness is about 200 nm, which is consistent with the result from SEM. Although some studies have reported the internal polar field in BiOCl,[14,15] the piezo-electric response of BiOCl has not been characterized. The PFM

[a] D. Shao, Dr. L. Zhang, Dr. S. Sun, Prof. W. Wang
State Key Laboratory of High Performance Ceramics and Superfine Micro-structure
Shanghai Institute of Ceramics
Chinese Academy of Sciences
1295 Dingxi Road, Shanghai 200050 (P. R. China) E-mail: wzwang@mail.sic.ac.cn

[b] D. Shao
University of Chinese Academy of Sciences Beijing 100049 (P. R. China)

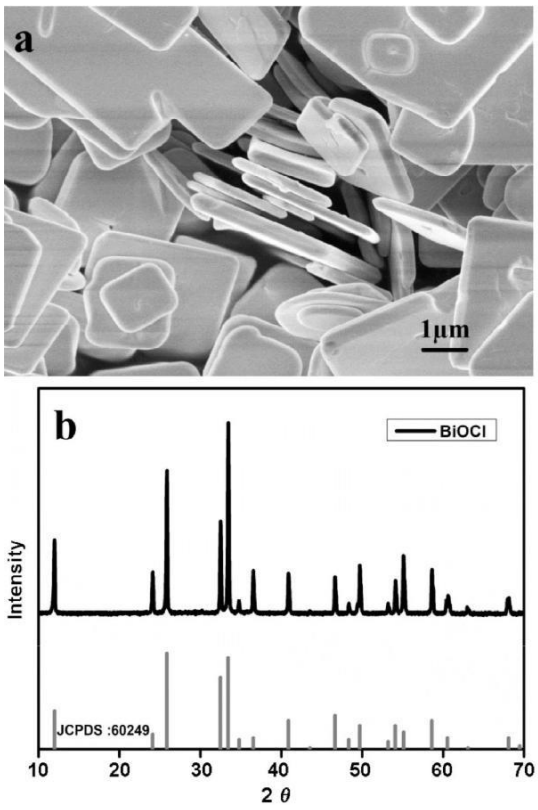

Figure 1. a) SEM image and b) XRD patterns of as-synthesized BiOCl.

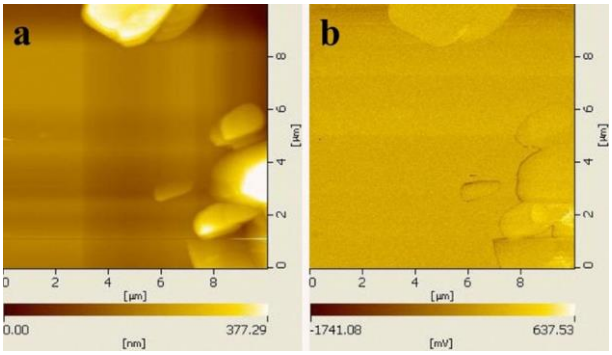

Figure 2. a) AFM and b) PFM images of as-synthesized BiOCl.

image of BiOCl revealed the piezoelectric response was indeed created from BiOCl microplates at an external load.

On the basis of the piezoelectric response of BiOCl micro-plates, we performed the experiment of generating H_2O_2 over BiOCl with ultrasonic waves. Without any scavengers, the ultra-sonic energy-driven generation of H_2O_2 in the presence of BiOCl was realized. As shown in Figure 3, the generation rate of H_2O_2 could reach 28 mmol $h^{@1}$, which is above the average level achieved by powdered water splitting photocatalysts (summary of representative experiments for generating H_2O_2 through a solar-to-chemical process is shown in the Support-ing Information, Table S1). The amount of H_2O_2 continuously increased with time without a noticeable decay. The X-ray dif-fraction (XRD) and UV/Vis diffuse reflectance spectra of BiOCl

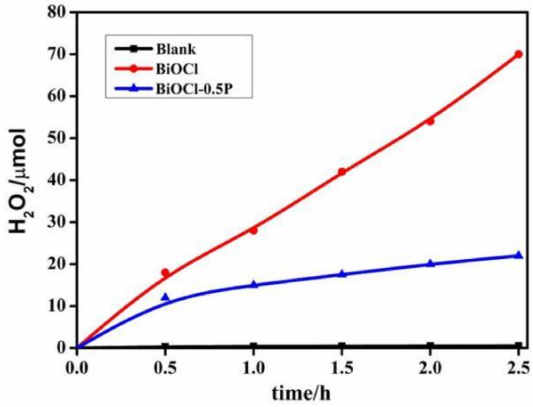

Figure 3. H_2O_2 generation upon irradiation of ultrasonic waves. The black line represents no addition of BiOCl; red line represents applying the 100 % power of ultrasonic machine; blue line represents applying the 50 % power of ultrasonic machine.

before and after use remain unchanged, indicating the stability of BiOCl (as shown in the Supporting Information, Figure S1). It was found that the generation rate of H_2O_2 was negligible (0.5 mmol $h^{@1}$) in the absence of BiOCl. Such phenomena indi-cated that BiOCl was necessary for generating H_2O_2. When the power of ultrasonic waves was adjusted to 50 % of the full power, the generation rate of H_2O_2 decreased to 3 mmol $h^{@1}$ except for the initial 30 min. The lower power contributed to much lower generation rate of H_2O_2, indicating that the ampli-tude of ultrasonic waves was a key factor for the generation of H_2O_2, because for piezoelectric materials the voltage output is proportional to the amplitude of external ultrasonic waves.[17]

We obtained H_2O_2 from the suspension of BiOCl with ultra-sonic waves, but the mechanism is not clear. There are two possible reactions for generating H_2O_2. One consists of O_2 re-acting with H_2O and finally transforming into H_2O_2 [Eq. (1)] and the other consists of H_2O decomposing into H_2 and H_2O_2 [Eq. (2)].

$$2H_2O + O_2 \xrightarrow{\text{BiOCl/ultrasonic}} 2H_2O_2 \qquad (1)$$

$$2H_2O \xrightarrow{\text{BiOCl/ultrasonic}} 2H_2 + O_2 \qquad (2)$$

To ascertain the role of O_2 for generating H_2O_2, we per-formed an experiment of controlling the atmosphere in a sealed double-deck glass vessel with ultrasonic waves for 5 h. The results are shown in Figure 4: when the atmosphere was high-purity N_2, a small amount of H_2 showing a linear relation-ship with time could be detected and the amount of H_2O_2 was 1.68 mmol; when the atmosphere was high-purity O_2, H_2 could not be detected and the amount of H_2O_2 was 28.5 mmol. When BiOCl was absent, H_2 and H_2O_2 could not be detected in any atmosphere. In view of the amount of H_2O_2 produced with BiOCl in the atmospheres of high-purity N_2 and O_2, it could be concluded that the O element of the obtained H_2O_2 was mainly from O_2. The competition of generation of H_2O_2 and H_2 may be attributed to the different reduction potentials, be-cause the redox potential of H_2O_2/O_2 (0.68 V, pH 0)[4b] is more positive than that of H_2/H^+ (0.00 V, pH 0)[16] and electrons

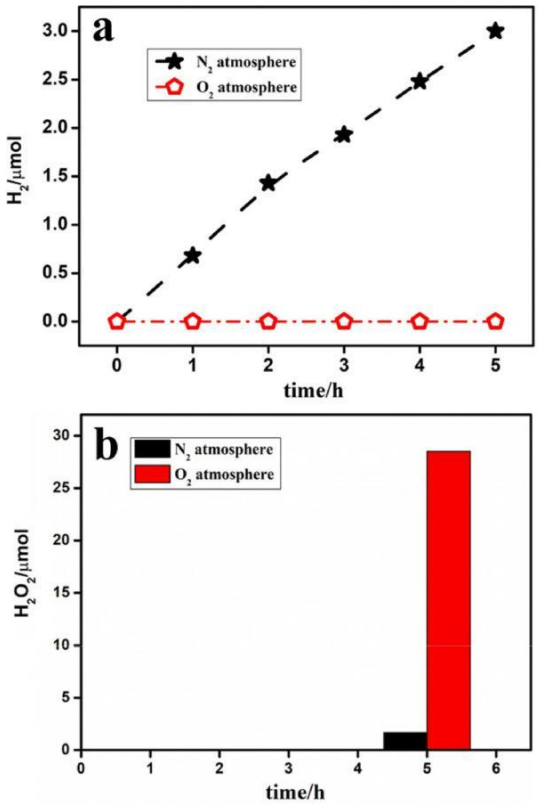

Figure 4. a) H_2 generation at high pure N_2 and O_2 atmosphere and b) H_2O_2 generation at high pure N_2 and O_2 atmosphere in suspension of BiOCl with ultrasonic waves.

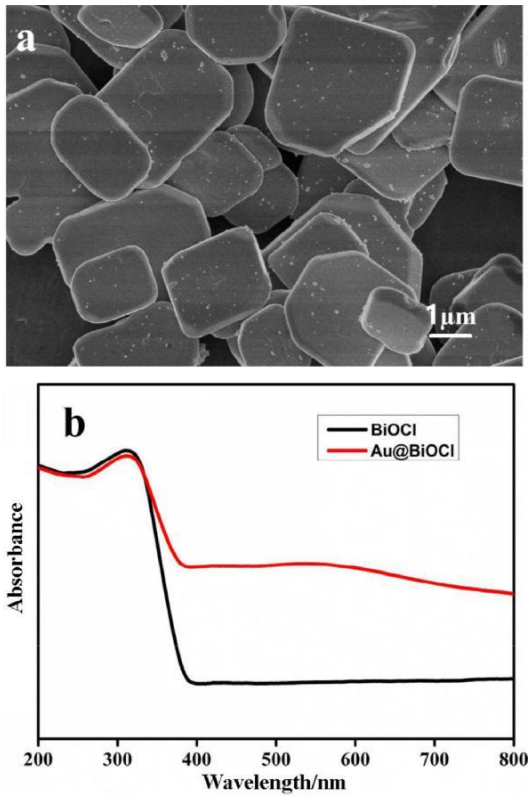

Figure 5. a) SEM image of Au@BiOCl and b) UV/Vis diffuse reflectance spec-tra of as-prepared sample.

prefer to reduce O_2. An experiment to determine the generation and diffusion of electrons was therefore needed.

To verify that the electrons induced by the piezoelectric effect over BiOCl with ultrasonic waves can transfer to the sur-face and participate in chemical reactions, a Au-deposition experiment was performed. In general, the deposition of noble metals is realized by the reduction reaction induced by photo-generated electrons or reducing agents. From a thermodynamics point of view, the potentials of ORR and the hydrogen evolution reaction are far more negative than the reduction po-tential of $HAuCl_4$, therefore, depositing Au on BiOCl in the sus-pension of BiOCl and $HAuCl_4$ through the piezo-catalytic effect should be feasible. With ultrasonic waves, the suspension of BiOCl and $HAuCl_4$ gradually turned to purple and finally to black, which was an indication of the the presence of metallic Au. The UV/Vis diffraction spectrum showed the extended ab-sorption edge of Au@BiOCl. An extra absorption peak at 550 nm in contrast to pure BiOCl was ascribed to the deposi-tion of Au nanoparticles (Figure 5 b). An SEM image of Au@-BiOCl is shown in Figure 5 a. It clearly shows that Au nanoparti-cles were randomly deposited on the surface of BiOCl, and the size of Au nanoparticles ranges from 20 to 100 nm.

The suspension only contains BiOCl, H_2O, and O_2. Therefore, there are two possible pathways of consuming holes (charge carriers) induced by the piezoelectric effect: one is the oxida-tion of BiOCl and the other is the oxidation of H_2O. If the holes are consumed by decomposing BiOCl, the whole reaction for-mula should be as shown in Equation (3). However, producing 70 mmol H_2O_2 (as shown in Figure 3) will consume 280 mmol BiOCl, which is contradictory with the practical usage of BiOCl (50 mg, 191 mmol). The characterization of BiOCl before and after use also verified that BiOCl had good stability under ultra-sonic waves (as shown in the Supporting Information, Fig-ure S1). In view of the thermodynamics, H_2O has a more nega-tive oxidation potential (1.23 V, pH 0) than $Cl^{@}$ (1.36 V, pH 0), so the holes prefer to oxidize H_2O. As a result, the induced holes were consumed by oxidizing H_2O.

ultrasonic

$$4BiOCl + 3H_2O + O_2 \rightarrow 2Bi_2O_3 + 4HClO + H_2O_2 \quad (3)$$

The mechanical-energy-driven generation of H_2O_2 may be derived from two pathways: one is the ORR [Eq. (4), Eq. (5)] and the other is both of ORR and the oxidation of H_2O [Eq. (6)].

$$e^{@} + O_2 \rightarrow O_2C^{@} \quad (4)$$

$$O_2C^{@} + e^{@} + H^{+} \rightarrow H_2O_2 \quad (5)$$

$$2H_2O + 2h^{+} \rightarrow H_2O_2 + 2H^{+} \quad (6)$$

To confirm the intermediate products in the H_2O_2 genera-tion, experiments of addition of scavengers were performed (Figure 6). Isopropanol (IPA) is a common OHC scavenger and benzoquinone (BQ) is a common $O_2C^{@}$ scavenger.[18] With the addition of IPA, the amount of H_2O_2 increased about three

Figure 6. H_2O_2 generation over BiOCl with addition of different scavengers.

times in contrast to the suspension of BiOCl without IPA, which indicated that the induced holes could oxidize H_2O into OHC and the formed H_2O_2 was not from the oxidation of H_2O. The existence of OHC was further confirmed by the degradation of the organic pollutant rhodamine B (RhB, for details, please refer to the Supporting Information, Figure S2) However, with the addition of BQ, the generation rate of H_2O_2 decreased to zero, which indicated that the electrons were the key for gen-erating H_2O_2 and $O_2C^{@}$ was the intermediate of the formed H_2O_2. These results confirm that H_2O_2 was generated through the ORR by the electrons induced by the piezoelectric effect.

On account of the above results and previous reports of the piezo-catalytic effect,[7, 9, 19–21] we propose a mechanism to illus-trate the process H_2O_2 generation. When ultrasonic waves are applied to BiOCl, an electric field along <001 > will be gener-ated. The as-generated electric field can induce and separate the electron–hole pairs, as shown in Equation (7). Next, the O_2 traps the electron and forms $O_2C^{@}$, as shown in Equation (8). Simultaneously, the water will be transferred to OHC and H^+ by interacting with holes, as shown in Equation (9). Then, protons and electrons interact with the $O_2C^{@}$ to form H_2O_2, as shown in Equation (10). One of the possible ways of consuming OHC is when it receives one electron and H^+ to regenerate H_2O, as shown in Equation (11); another is when four OHC convert into H_2O and O_2, as shown in Equation (12).

$$BiOCl + ultrasonic \xrightarrow{piezoelectricresponse} h^{+} + e^{@} \quad (7)$$

$$O_2 + e^{@} \rightarrow O_2C^{@} \quad (8)$$

$$H_2O + h^{+} \rightarrow OHC + H^{+} \quad (9)$$

$$O_2C^{@} + e^{@} + 2H^{+} \rightarrow H_2O_2 \quad (10)$$

$$OHC + H^{+} + e^{@} \rightarrow H_2O \quad (11)$$

$$4\,OHC \rightarrow 2\,H_2O + O_2 \quad (12)$$

In summary, the oxygen reduction reaction (ORR) for gener-ating H_2O_2 through the piezo-catalytic effect was realized over BiOCl with ultrasonic waves. The piezoelectric response of BiOCl was first characterized by piezoresponse force microsco-py (PFM). Under air atmosphere, the generation of H_2O_2 can reach 28 mmol $h^{@1}$. The experiment of controlling the atmos-phere indicated that H_2O_2 was mainly formed from O_2 and H_2O. Experiments of Au deposition and addition of scavengers confirm that the formed H_2O_2 was derived from ORR by the electrons induced by the piezoelectric effect. Based on these results and previous reports, a mechanism was proposed, with ultrasonic waves over BiOCl driving the electrons interact with H_2O and O_2 to generate H_2O_2. This research provides a safe and green method of generating H_2O_2 by harvesting ultrasonic energy and may facilitate the energy and avoid environmental issues.

Experimental Section

Materials: All chemicals were of analytical grade purity obtained from Sinopharm Chemical Reagent Co. Ltd and used as received without further purification.

Synthesis of BiOCl: In a typical procedure, $Bi(NO_3)_3{\cdot}5\,H_2O$ (2 mmol) and KCl (2 mmol) were added in distilled water (30 mL) at room temperature with continuous stirring. The suspension was stirred for 1 h and then poured into a 50 mL Teflon-lined stainless auto-clave. The autoclave was allowed to be heated at 160 8C for 24 h, and then air-cooled to room temperature. The resulting precipi-tates were collected and washed with ethanol and deionized water for several times to remove residual ions.

Au@BiOCl: The BiOCl (50 mg) and $HAuCl_4$ (1 mg) were added to pure water (100 mL) in a Pyrex glass of 500 mL and thoroughly mixed by stirring. After 10 min, the glass was placed in an ultrason-ic cleaner (SK2200HP).With stirring, the suspension was treated by ultrasonic waves for 60 min. The purple-black resulting products were centrifuged and washed with pure water. The above sample was then dried at 60 8C for 4 h for further characterization.

Piezo-catalytic performance measurement: Normally, BiOCl (0.05 g) was dispersed in pure water (100 mL). The generation of H_2O_2 in air was done in a Pyrex glass of 500 mL in an ultrasonic cleaner (SK3200HP) with stirring by a power-driven stirrer of D2004W. The power of ultrasonic cleaner was 150 W and the fre-quency 53 KHz. The experiment in high-purity N_2 and high-purity O_2 atmosphere was performed, respectively in a sealed double-deck Pyrex glass of 600 mL in the ultrasonic cleaner. The amount of H_2O_2 in solution was determined by the titanium sulfate spectro-photometric method using a UV/Vis spectrophotometer (Hitachi 3010) equipped with an integrating sphere. Generated H_2 was de-tected by an online gas chromatograph (Tianmei, GC-7890, TCD, Ar carrier). For the experiment with addition of scavengers, IPA (10 mm) was selected as OHC scavenger, BQ (0.1 g) was selected as $O_2C^{@}$ scavengers. RhB was selected as a model pollutant. The con-centration of RhB was 10 mg $L^{@1}$.

Characterization methods: The samples were characterized by XRD on a Rigaku powder diffractometer. The samples were scanned using CuK_a radiation with an operating voltage of 30 kV and operating current of 100 mA. The scan rate of 48 $min^{@1}$ was ap-plied to record the patterns in the range of 10–708. UV/Vis diffuse reflectance spectra were recorded on an UV/Vis spectrophotometer (Hitachi 3010) equipped with an integrating sphere. The morpholo-gies of the as-prepared samples were investigated by SEM (Hitachi S4800). The piezoelectric response of as-prepared sample was char-acterized by an AFM (SPA-300HV) equipped with a ferroelectric test system. In a typical procedure of sample preparation, for the

PFM test, a drop of the suspension of BiOCl dispersed on the Si substrate coated Pt by pulsed laser deposition (PLD).

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (51772312, 21671197, 51472260) and the research grant (16ZR1440800) from Shanghai Science and Technology Commission

Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth oxychloride · hydrogen peroxide · oxygen reduction reaction · piezo-catalytic effect · piezoelectric response

[1] J. M. Campos-Martin, G. Blanco-Brieva, J. L. G. Fierro, Angew. Chem. Int. Ed. 2006, 45, 6962 – 6984; Angew. Chem. 2006, 118, 7116 – 7139.

[2] a) K. Mase, M. Yoneda, Y. Yamada, S. Fukuzumi, Nat. Commun. 2016, 7, 11470; b) S. Kato, J. Jung, T. Suenobua, S. Fukuzumi, Energy Environ. Sci. 2013, 6, 3756 – 3764; c) Y. Yamada, M. Yoneda, S. Fukuzumi, Chem. Eur. J.2013, 19, 11733 – 11741.

[3] W. C. Hou, Y. S. Wang, ACS Sustainable Chem. Eng. 2017, 5, 2994 – 3001.

[4] a) D. Tsukamoto, A. Shiro, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T.Hirai, ACS Catal. 2012, 2, 599 – 603; b) Y. Kofuji, Y. Isobe, Y. Shiraishi, H. Sakamoto, S. Tanaka, S. Ichikawa, T. Hirai, J. Am. Chem. Soc. 2016, 138, 10019 – 10025; c) K. Mase, M. Yoneda, Y. Yamada, S. Fukuzumi, ACS Energy Lett. 2016, 1, 913 – 919; d) S. Li, G. Dong, R. Hailili, L. Yang, Y. Li, F. Wang, Y. Zeng, C. Wang, Appl. Catal. B 2016, 190, 26 – 35; e) S. Zhao, X. Zhao, H. Zhang, J. Lia, Y. Zhu, Nano Energy 2017, 35, 405 – 414.

[5] Y. Xi, J. Wang, Y. Zi, X. Li, C. Han, X. Cao, C. Hu, Z. Wang, Nano Energy 2017, 38, 101 – 108.

[6] C. F. Pan, M. X. Chen, R. M. Yu, Q. Yang, Y. F. Hu, Y. Zhang, Z. L. Wang, Adv. Mater. 2016, 28, 1535 – 1552.

[7] K. S. Hong, H. F. Xu, H. Konishi, X. C. Li, J. Phys. Chem. Lett. 2010, 1, 997 – 1002.

[8] Z. L. Wang, J. H. Song, Science 2006, 312, 242 – 246.

[9] a) J. M. Wu, W. E. Chang, Y. T. Chang, C. K. Chang, Adv. Mater. 2016, 28, 3718 – 3725; b) M. H. Wu, J. T. Lee, Y. J. Chung, M. Srinivaas, J. M. Wu, Nano Energy 2017, 40, 369 – 375; c) J. H. Lin, Y. H. Tsao, M. H. Wu, T. M. Wu, T. M. Chou, Z. H. Lin, J. M. Wu, Nano Energy 2017, 31, 575 – 581.

[10] M. B. Starr, J. Shi, X. Wang, Angew. Chem. Int. Ed. 2012, 51, 5962 – 5966; Angew. Chem. 2012, 124, 6064 – 6068.

[11] H. Lin, Z. Wu, Y. Jia, W. Li, R. K. Zheng, H. Luo, Appl. Phys. Lett. 2014, 104, 162907.

[12] Y. Feng, L. Ling, Y. Wang, Z. Xu, F. Cao, H. Li, Z. Bian, Nano Energy 2017, 40, 481 – 486.

[13] T. P. Fellinger, F. Hasche, P. Strasser, M. Antonietti, J. Am. Chem. Soc. 2012, 134, 4072 – 4075.

[14] K. L. Zhang, C. M. Liu, F. Q. Huang, C. Zheng, W. D. Wang, Appl. Catal. B 2006, 68, 125 – 129.

[15] L. Zhang, W. Wang, S. Sun, D. Jiang, E. Gao, Appl. Catal. B 2015, 162, 470 – 474.

[16] L. Zhang, Z. Han, W. Wang, X. Li, Y. Su, D. Jiang, X. Lei, S. Sun, Chem. Eur. J. 2015, 21, 18089 – 18094.

[17] Y. Kim, K. Y. Lee, S. K. Hwang, C. Park, S. W. Kim, J. Cho, Adv. Funct. Mater. 2014, 24, 6262 – 6269.

[18] E. P. Gao, W. Z. Wang, Nanoscale 2013, 5, 11248 – 11256.

[19] H. Huang, S. Tu, C. Zeng, T. Zhang, A. H. Reshak, Y. Zhang, Angew. Chem. Int. Ed. 2017, 56, 11860 – 11864; Angew. Chem. 2017, 129, 12022 – 12026.

[20] S. Lan, J. Feng, Y. Xiong, S. Tian, S. Liu, L. Kong, Environ. Sci. Technol. 2017, 51, 6560 – 6569.

[21] S. Hong, H. F. Xu, H. Konishi, X. C. Li, J. Phys. Chem. C 2012, 116, 13045 – 13051.